SPLITTING OF SPECTRAL LINES AT SCATTERING BY LIQUIDS *

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ABSTRACT. The fine structure of the Rayleigh line due to the molecular scattering in liquids has been investigated with a F. P. etalon and the two fine structure components are identified, the higher component reported by Gross being absent. The question of the reality of the red shift of the Rayleigh line observed by Cabannes and his co-workers with a F. P. etalon has also been examined and it has been shown that there is no such red shift.

The observed values of the shifts of the displaced components from the central ones were always found to be greater than the values calculated from the Brillouin's equation.

The dependence of the frequency shifts of the splitted components from the central main-lines, on the following has also been investigated :-

(*a*) The frequency of the incident light.

(*b*) Angle of the scattering.

The influence of temperature on the splitted components has also been examined and it is found that the splitted components become fainter and broader, gradually merging with the central undisplaced components as the temperature of the liquid is raised. The intensity of the central components also is gradually increased. On the other hand, opposite effects were observed on lowering the temperature of the liquid.

The state of polarisation of the three components was also examined. The results indicate that all of them are completely polarised

INTRODUCTION

It is now well known that the molecules of a gas are capable of three types of movements, namely, translational, rotational and vibrational movements. When a beam of monochromatic light passes through a gaseous medium and is scattered by it, each of the aforesaid movements are capable of giving rise to changes of frequency in the scattered radiation, *viz.*, a Doppler effect due to the translatory motion of the molecules of the gases and Raman effect due to their rotations and vibrations respectively. The Doppler effect, generally, shows its presence in the form of a simple Maxwellian broadening of the lines in the scattered spectrum; the broadening would be a function of the angle of observation, being zero in the direction of the incident light and maximum in the reverse direction.

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But when we pass from the case of a gaseous medium to that of a liquid, various complications arise from the fact that the positions and the velocities of the molecules are no longer distributed "at random" and as such it is not possible to regard the molecules as being completely independent scattering centres. The nature of the Doppler effect expected in such a medium would naturally be complex. An insight into the nature of the Doppler effect in liquids was furnished by the theory of the light scattering originally put forward by Einstein.[1] In his theory the molecular structure of the scattering medium is ignored and fluctuation of density are regarded as arising in it from the presence of sound waves of various wavelengths associated with the thermal energy of the medium. These sound waves produce stratifications in the optical density of the medium and give rise to a selective scattering in directions determined by the wavelength of the incident light and of the reflecting sound wave.

Later Brillouin [2] pointed out that on this view, the light reflected by the trains of sound waves should exhibit a Doppler effect which would take the simple form of a doubling of the lines in the incident spectrum, the frequency of the splitted components being given by the relation

$$\nu=\nu_0 \pm 2\nu_0 \frac{v}{c} \sin \theta/2 \qquad \ldots \qquad (1)$$

where v and c are the velocity of the sound and of light in the medium, θ the angle of scattering, ν_0 the frequency of the incident light.

A similar relation was also deduced by Mandelstam[3] from a somewhat different consideration. The possibility of a change in light frequency according to the equation of Brillouin was also pointed out by Rocard & Bogros.[4]

During the last few years a large number of workers reported the results of their investigations on the subject of the fine structure of the Rayleigh radiation in liquids, but their results are highly contradictory as will be evident from the following. Cabannes,[5] while investigating the nature of the Rayleigh scattering in liquids and gases with a Fabry-Parot etalon, claimed to have observed a shift of the Rayleigh lines at scattering towards the greater wavelength, generally designated as "Cabannes red shift." Very similar results were also obtained by Vacher [6] with a F. P. etalon. Later Gross,[7] working with a Lummer Plate, found the splitting of the incident spectral line at scattering by the liquids, *i.e.*, a line in the position of the incident radiation accompanied by a series of components symmetrically situated on either side of the central line. The frequencies of these components were found to satisfy the relation

$$\nu=\nu_0 \pm 2n\nu_0 \frac{v}{c} \sin \theta/2 \qquad (2)$$

where $n = 1, 2, 3 \ldots\ldots$, and ν_0 the frequency of the incident radiation. But Rafalowski,[8] working with Lummer Plate, was unable to observe either the "Gross splitting" or the "Cabannes red shifts." Mayer and Ramm [9] and later Ramm,[10] working with an etalon grating, claimed to observe the first Gross components on either side of the central undisplaced line but could not detect the other components as reported by Gross. In view of the unsatisfactory state of the subject we undertook a systematic study of the subject using a Fabry-Parot etalon. The choice of this instrument was guided by the fact that those who used the same were unable to observe the Gross splitting but instead some found the Cabannes red shift—a fact which is rather very perplexing. In our investigation,[11] in all the cases of the liquids we have found the splitting as reported by Gross, the first components corresponding to $n = \pm 1$ in (2) being alone present. We were unable to find either the higher components or the red shift. Simultaneously with our investigation Rao[12] and Khvostikov[13] all independently claimed to have been able to observe the Gross splitting with a Fabry-Parot etalon.

The present paper gives a detailed report of our investigation under the following heads :—

A. How far the value of the shifts $\nu - \nu_0$ as observed agree with the value calculated from the Brillouin's equation.

B. Dependence of $\Delta\nu = \nu - \nu_0$ on the angle of scattering.

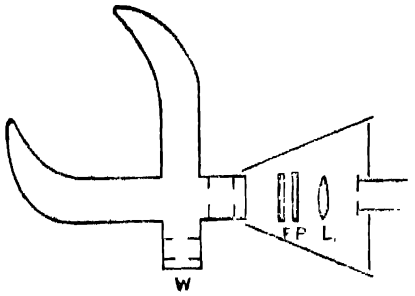
C. Dependence of $\Delta\nu$ on the wave-length of the incident light.

D. Influence of temperature.

E. The nature of the polarisation of the splitted components as well as of the central undisplaced components.

EXPERIMENTAL ARRANGEMENTS

The experimental arrangement, at first adopted in our experiment, is practically the same as that employed by Cabannes and his co-workers. The arrangement is shown in figure 1 which will speak itself. Light from a cooled mercury arc is condensed with a lens through the window w, on to the centre of two horn-shaped cross-tubes containing the liquid under investigation. The radiation scattered at right angles condensed on to the slit of a spectrograph by lenses after has passed through the Fabry-Parot etalon. In the cases of the observations at angles 135° and 45° cross-tubes of the forms given in figurss 2 and 3 were employed. For the observations at 180°, we have followed the experimental arrangements of Mayer and Ramm.[9, 10]



Spectrograph

FIGURE 1.

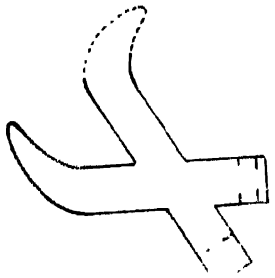


FIGURE 2.

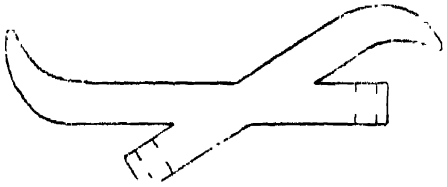


FIGURE 3.

In some cases we also employed the following arrangement. The repeatedly vaccum distilled liquid was contained in a horizontal Wood tube. A parallel beam of light from a horizontal mercury arc lamp was made to illuminate the side of the Wood-tube along its axis by means of a big lens The interference rings system was focussed on to the slit of the spectrograph. In order to remove the possibility of stray light getting into the F. P. etalon a cone-shaped cap was placed on the observation side as shown in the figure. The Wood tube was surrounded by another tube and cold water at the laboratory temperature was continually circulated through the annular space by means of a small circulating pump in order to maintain the temperature of the liquid constant. We have employed the spectrograph in conjunction with the F. P. etalon because of its great advantage that the interference patterns of a number of lines could be photographed at a time on the same plate.

In the case of the polarisation measurements a large square-ended nicol is placed between the observation side of the cross-tube (Fig. 1) or the Wood tube and the F.P. etalon—the fringes being focussed on the slit of the spectrograph by another lens. Two separate spectra were recorded in each case, one with the nicol having its vibration axis vertical and another with the vibration axis horizontal.

The interference patterns of the three lines λ4358, 4078 and 4047A were examined and the displacements of the new-splitted components measured without any confusion arising from the presence of the hyperfine structures components.

HOW FAR THE VALUES OF THE SHIFT $\Delta\nu$ AGREE WITH THAT CALCULATED WITH HELP OF THE BRILLOUIN'S EQUATION ?

We have studied the scattered radiations with the F.P. etalon in the case of a large number of liquids—benzene, toluene, carbon tetrachloride, carbon disulphide, methyl alcohol, cyclohexane, cyclohexanol, etc., with a view to finding out how far the value of the shifts $\Delta\nu$ agree with those calculated from the Brillouin's formula. For if a complete agreement between the calculated and the observed value of the shifts $\Delta\nu$ be obtained, then this splitting of the spectral lines at scattering by liquids gives us an optical method for the determination of the velocity of sound in liquids.

In all the cases of the liquids—as already mentioned—we have found the splitting as reported by Gross, *the first component corresponding to* $n = \pm 1$ *being alone present.* The higher components observed by Gross were totally absent. *The Cabannes red shifts were also never observed.* The values of the shifts are given in the following table 1. The values of $\Delta\nu$ calculated from the Brillouin's equation

$$\Delta\nu = 2\nu_0 \frac{v}{V} \sin \theta/2$$

are also included in the tables

TABLE I

Angle of Observation $= \pi/2$

Wavelength of the incident light $= 4358$ Å

Liquids	$\Delta\nu$ in cm.$^{-1}$		
	Observed.	Calculated.	Difference.
Benzene	·237	·206	·031
Toluene ...	·235	·214	·021
Carbon tetrachloride ...	·177	·154	·023
Carbon disulphide ...	·239	·211	·028
Methyl alcohol ...	·194	·170	·024
Chlorobenzene	·237	·214	·023
Cyclohexane ...	·213	·192	·021
Cyclohexanol ...	·289	·265	·024

The values of $\Delta\nu$ as observed are always found to be greater than that calculated from the formula, the difference being shown in column 4. In these calculations the experimental values for the velocity of sound obtained chiefly by Kundt tube method were employed. The velocity of sound calculated from the coefficient of compressibility and density of the liquids also do not give values of $\Delta\nu$ which are in agreement with the observed values of $\Delta\nu$.

TABLE II

Angle of Observation $= \pi$
Wavelength of the incident light $= 4357$A

Liquid	$\Delta\nu$ in cm.$^{-1}$		
	Observed.	Calculated.	Differences
Benzene ..	·332	·295	·037
Carbon tetrachloride ...	·248	·211	·037

Such a difference between the observed and the calculated values has also been observed by Gross* and Mayer and Ramm with a Lummer Plate. But Rao working with F.P. etalon reported fair agreement within the errors of measurements. Their values are given below together with ours in table 3.

TABLE III

Benzene
Angle of scattering $= \pi$
Wavelength of the incident light $= 4358$A

Authors.	$\Delta\nu$ in cm.$^{-1}$		Difference.
	Calculated.	Observed.	
Mayer and Ramm ...	·295	·326	·031
Rao ...	,,	·306	·011
Mitra ...	,,	·332	·037

It is evident from the above table that our values agree with those of Mayer and Ramm rather than with Rao's.

* Gross in his earliest communication reported complete agreement between the calculated and observed values, but later on he observed a difference.

In all the cases of the liquids, there was a continuous background superimposed on the interference patterns. The intensity of this continuous background was most intense in the case of carbon disulphide and cyclohexanol and very feeble in the case of carbon tetrachloride. This intense continuous background radiation made the distinct reproduction of the spectrograms impossible.

The width of the displaced and unshifted components as well as their intensities were not the same for the different liquids. The width is less in carbon disulphide, carbon tetrachloride, toluene, which gave shifted components very distinct. Methyl alcohol, cyclohexanol and cyclohexane gave rather diffused components whereas the width in the case of benzene was midway between the aforesaid two classes. Here it is to be noted that we have been able to observe splitting in the case of viscous liquid, cyclohexanol, which is very significant in the face of the result obtained by the Raman and Rao [11] and by Raman and Venkataswaran.[15]

The intensities of the displaced components in the case of carbon tetrachioride were most intense.

According to the Brillouin theory, the central unmodified lines (corresponding to $n=0$ in equation 2) should not be present in the liquids. But they were observed in our investigations with all the liquids. The intensity of this central undisplaced component was most intense in the case of carbon tetrachioride, showing that its presence is not to be primarily ascribable to the optical anisotropy of the liquid.

DEPENDENCE OF THE SHIFT $\Delta\nu$ ON THE WAVELENGTH OF THE INCIDENT LIGHT

Brillouin theory points out that the frequency shifts should depend on the frequency of the incident light. Here we experimentally attempted to observe whether the shifts do depend on the incident frequency.

The following tables give the results of our investigation. It might be noted here in passing that our values of $\Delta\nu$ in the case of CCl_4 agree with those of Rao,[16] who has recently redetermined them using improved technique.

TABLE IV

Angle of scattering $= \pi$

Liquid.	Wavelength.	Observed.	Calculated.	Difference
Benzene	4358	·332	·295	·037
	4078	·348	·315	·033
	4047	·251	·318	·033
Carbont etrachloride	4358	·248	·321	·027
	4078	·258	236	·022
	4047	·264	238	·026

We have also calculated the differences of the shifts $\Delta\nu$ for $\lambda 4047$ and $\lambda 4358$ for benzene and carbon tetrachloride, the following gives the result.

TABLE V

Difference between the shifts $\Delta\nu$ for $\lambda 4047$ and 4358A

Angle of scattering $= \pi$

Liquid.	$\Delta\nu$ in cm.$^{-1}$	
	Observed.	Calculated.
Benzene	·019	·023
Carbon tetrachloride	·016	·017

Measurements were also made at 90° angle of scattering; the following gives the results of our measurements.

TABLE VI

Angle of scattering $= \pi/2$

Liquids.	Wavelength.	$\Delta\nu$ in cm.$^{-1}$ Observed.
Benzene ...	4358	·237
	4078	·249
	4047	·241
Carbon tetrachloride ..	4358	·177
	4078	·190
	4047	·194
Carbon disulphide ...	4358	·239
	4078	·259
	4047	·264
Cyclohexane ...	4358	·213
	4078	·224
	4047	·231

The foregoing results conclusively show experimentally that the frequency shifts of the splitted Gross components depend on the frequency of the incident light. Here also we find that the calculated and observed values do not agree whatever be the incident wavelength, and the difference between the calculated and observed values is nearly the same for all the wavelengths of the incident light.

VARIATION OF THE SHIFTS $\Delta\nu$ ON THE ANGLE OF SCATTERING

In our present investigation we have also examined the scattered radiation at the different angles of scattering in order to study the variation of the shifts with the angles of scattering. We may here point out that the Brillouin's equation points out that $\Delta\nu$ varies with the angle of scattering.

The following table gives the values of the shifts for the four angles of scattering. We do here also find a great dependence of the amount of the shifts of the Gross components on the angle of the scattering, as would be expected from the Brillouin's equation.

TABLE VII

Wavelength of the incident light = 4358A

Liquids.	$\Delta\nu$ in cm.$^{-1}$		Observed.		$\frac{\Delta\nu_{180^\circ}}{\Delta\nu_{90^\circ}}$	
	180°	135°	90°	45°	Observed.	Calculated
Benzene	·332	·289	·237	·149	1·42	1·42
Carbon disulphide	·328	·292	·239	150	1 38	1·42
Carbon tetrachloride	·248	—	·177	—	1·40	1·42
Chlorobenzene	·335	·268	·237	—	1·41	1·42
Toluene	·316	·270	·235	—	1·35	1·42
Methyl alcohol	·274	—	·194	—	1·41	1·42
Cyclohexane	·302	—	·213	—	1·41	1·42
Cyclohexanol	·407	·318	·289	—	1·41	1·42

According to the formula the ratio of the amounts of the shifts at 180° and 90° is equal to the ratio of the sine of 90° and 45°, *i.e.*, $\frac{\Delta\nu_{180^\circ}}{\Delta\nu_{90^\circ}} = \frac{\sin 90^\circ}{\sin 45^\circ} = 1{\cdot}42$; this fairly agrees with the values calculated from the observed shifts, as is shown in the aforesaid table.

INFLUENCE OF TEMPERATURE

We have also examined in our present investigation the influence of temperature on the Doppler components. Besides the data collected by Rao and Raman[17] and Rao [18] very little work seems to have been done in this direction. Moreover their results are more or less of qualitative nature. In view of the expectation that the results obtained in the study of the influence of temperature might lead to interesting points we carried out an investigation on the influence of temperature on the Cross components in benzene, carbon tetrachloride, toluene.

In the case of the present measurements, the experimental arrangements are as follows. The liquid under observation was contained in the wood tube, which was contained in a bath, the temperature of which can be varied at ease.

For the measurements at the higher temerature the liquid (water) in the bath was heated electrically by a small nichrome spiral immersed in it. By regulating the current through the nichrome wire, the temperature of the bath may be made constant to any desired point. In case of the low temperature measurements, the bath contained iced water. An accurate thermometer in the wood tube served to measure the temperature Our results are summarised below

The spectrum of the light scattered by the aforesaid liquid at the ordinary temperature (28°-30° C) shows the Doppler components more or less distinctly on either side of the central unshifted line when examined through the F P. etalon in all the cases of the liquids examined. But as the temperature is gradually raised the following changes take place :—

(*a*) The amount of the shifts $\Delta\nu$ decreases gradually.

(*b*) The Doppler components become fainter and broader, ultimately merging with the central component.

(*c*) The intensity of the central components gradually increases.

On the other hand, when the temperature is gradually lowered the following opposite changes were observed :—

(*a*) The amount of the shifts increases gradually.

(*b*) The Doppler component, on either side of the central line, become more sharp and intense.

(*c*) The intensity of the central camponent gradually decreases.

ON THE POLARISATION OF THE DOPPLER COMPONENTS

In our present investigation we have measured the state of polarisation of the splitted as well as of the undisplaced component in the case of the liquids cyclohexane, cyclohexanol, methyl alcohol.

Previously, Gross [19] also investigated the nature of the polarisation of the displaced and undisplaced components in the case of carbon tetrachloride and benzene. He found that while the two Brillouin components were completely polarised, as is to be expected theoretically, the central undisplaced component was also completely polarised. His conclusion was later confirmed by Rao.[20]

In our investigations in all the liquids examined we observed that all the three components are completely polarised, as was reported by the aforesaid workers.

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